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Effect of photoreactivity of polyimide on the molecular orientation of liquid crystals on photoreactive polymer/polyimide blends

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We prepared blend alignment layers from polymethacrylate with coumarin side chains (PMA-*g*-coumarin) and polyimides for the orientation of liquid crystals (LCs) using linearly polarized ultraviolet (UV) irradiation. We used two different polyimides, namely 4,4′-(hexafluoro-isopropylidene) diphthalic anhydride-3,5-diamino-benzoic acid (6FDA-DBA) and pyromellitic dianhydride-4,4′-oxydianiline (PMDA-ODA). It was found that the molecular orientation of the LC depended on the type of polyimide in the blend alignment layer. The thermal stability of the LC orientation was enhanced regardless of the type of polyimide, while the direction of LC orientation was different for each type of polyimide. The photoreactivity of the polyimide was a very important factor in determining the molecular orientation of the LC on the blend alignment layer. This may be attributed to the different mechanisms of LC orientation on PMA-*g*-coumarin and polyimide induced by the polarized UV irradiation. The direction of the LC orientation could be changed by controlling the photoreaction of the polyimides using the appropriate UV filter for the polarized UV irradiation.

1. Introduction

In order to align liquid crystal (LC) molecules, the process of rubbing the surface of a polyimide film is usually adopted in manufacturing liquid crystal displays (LCDs). However, this process has problems such as the generation of static charge, dust, or scratches caused by rubbing. Therefore, establishing a rubbing-free method is an important target in overcoming these problems arising from the rubbing process. LC alignment using ultraviolet (UV) exposure is a promising candidate as a non-rubbing method [1–4]. Photo-alignment layers made from photoreactive polymers with vinylcinnamate and coumarin have shown good LC alignment [3–7], but their thermal stability was poor. In order to enhance the thermal stability of the LC alignment layer, we have previously reported a method using polyimide to enhance the thermal stability of LC alignment layers of polyvinylcinnamate [8, 9].

In this work, we have introduced polyimide into a photopolymer based on coumarin in order to improve the thermal stability of the LC alignment layer. We blended two different polyimides, 6FDA-DBA and PMDA-ODA, with a photopolymer based on coumarin, specifically a polymethacrylate with coumarin side chains (PMA-*g*-coumarin) [4]. We investigated the effect of polyimide on the LC alignment properties on the blend alignment layers. We compared the photoreactivity of PMA-*g*-coumarin and polyimides and related the difference of photoreactivity to the direction of LC alignment on the blend alignment layers. We also controlled the polyimide photoreaction by using the appropriate UV filters and investigated the relationship between the degree of photoreaction and the LC alignment properties on the blend alignment layers.

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2. Experimental

2.1. *Materials*

Methacryloyl chloride, 7-hydroxycoumarin, 2,2′-azobisisobutyronitrile (AIBN), 4,4′-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA), 3,5-diamino benzoic acid (DBA), pyromellitic dianhydride (PMDA), 4,4′-oxydianiline (ODA), and isoquinoline were purchased from Sigma-Aldrich Chemicals and used without further purification. Nematic liquid crystal E7 was purchased from Merck.

2.2. *Synthesis of polymethacrylate with coumarin side chains*

Methacryloyl chloride was added to a pyridine solution of 7-hydroxycoumarin and the solution was stirred at room temperature for 1 h. The mixture was poured into water and the precipitate was filtered and dried in vacuum at room temperature. This monomer and AIBN were dissolved in *N*,*N*-dimethylformamide (DMF) and the solution was heated at 60°C for 10 h under nitrogen. The viscous solution was poured into methanol to separate a polymer which was purified by reprecipitation from methanol and dried in vacuum at 80°C. Figure 1 (*a*) shows the chemical structure of the PMA-*g*-coumarin.

2.3. *Synthesis of polyimides*

A *m*-cresol solution of DBA was stirred for 1 h under nitrogen, and an equimolar amount of 6FDA was added to the reactor. After a viscous solution was obtained, the reaction temperature was raised to 180°C and a catalytic amount of isoquinoline added to the mixture to accelerate the conversion of the amic acid group to the imide group. The reaction proceeded for 12 h under nitrogen. After completion of the imidization reaction, the resulting solution was washed several times with methanol and diethyl ether and dried under vacuum at 100°C for 12 h.

PMDA-ODA polyamic acid, the precursor of PMDA-ODA polyimide, was synthesized by adding an equimolar amount of PMDA to an *N*-methyl-2-pyrrolidone (NMP) solution of ODA mixture at room temperature under nitrogen. The solution was stirred for 24 h at room temperature; it was then poured into excess methanol. The precipitate was filtered and dried in vacuum at room temperature. PMDA-ODA polyamic acid was thermally imidized during the thermal curing of the spin-coated cast. Figures 1 (*b*) and 1 (*c*) show the chemical structures of 6FDA-DBA, and PMDA-ODA, respectively.

2.4. *Spectroscopic measurements*

UV spectra were recorded with a UV-visible spectrophotometer (UV-1601, Shimadzu). All measurements were made with quartz slides as substrates. The uncoated part of quartz slide was used as reference.

2.5. *Preparation of alignment layers*

NMP solutions of PMA-*g*-coumarin and polyimide (2 wt%) were mixed in fixed weight ratio (10/0, 7/3) and spin-coated onto the glass substrate at 1800 rpm. The cast was prebaked at 60°C for 30 min and the thermal curing of the cast was then conducted at 200°C for 1 h. After annealing, the photoreaction of coumarin and polyimide was carried out by irradiating the polymer thin film with polarized UV light. This was obtained by passing light from a 300 W high pressure mercury arc (Oriel) through a UV linear dichroic polarizer (27320, Oriel) and a UV filter 59800 (Oriel) onto the polymer thin film. UV filter 59610 (Oriel) was used for modifying the wavelength band of polarized UV. The intensity of the UV irradiation, measured using a UV detector (UIT-150, Ushio), was 4 mW cm^{-2}. For the generation of a certain pretilt angle of the nematic LC, the alignment layers were exposed to the polarized UV oblique to the alignment layers [4].

2.6. *Preparation of LC cells*

A homogeneously aligned LC cell was constructed by sandwiching nematic LC (E7) between a pair of glass substrates coated with a thin film of alignment materials. The LC layer thickness was adjusted by using a styrene bead of 8 μm diameter for measuring the order parameter and by using adhesion tape of 50 μm thickness for pretilt angle measurement. E7 liquid crystal was injected into the cell via capillary action in the isotropic phase.

2.7. *Determination of LC alignment*

The director of the nematic LC in the cell was determined from the dichroic absorption of a dichroic dye (disperse blue 14) in the nematic LC. A small amount of the dichroic dye shows strong absorption at 653 nm. From the angular dependency of the absorbance at 653 nm in the polarized UV spectra of the LC cell, the distribution of LC director could be determined.

2.8. *Pretilt angle measurement*

The pretilt angle of the nematic LC was measured by means of crystal rotation method as described elsewhere [10]. From the plot of transmittance versus the incidence angle of a He-Ne laser beam passing through

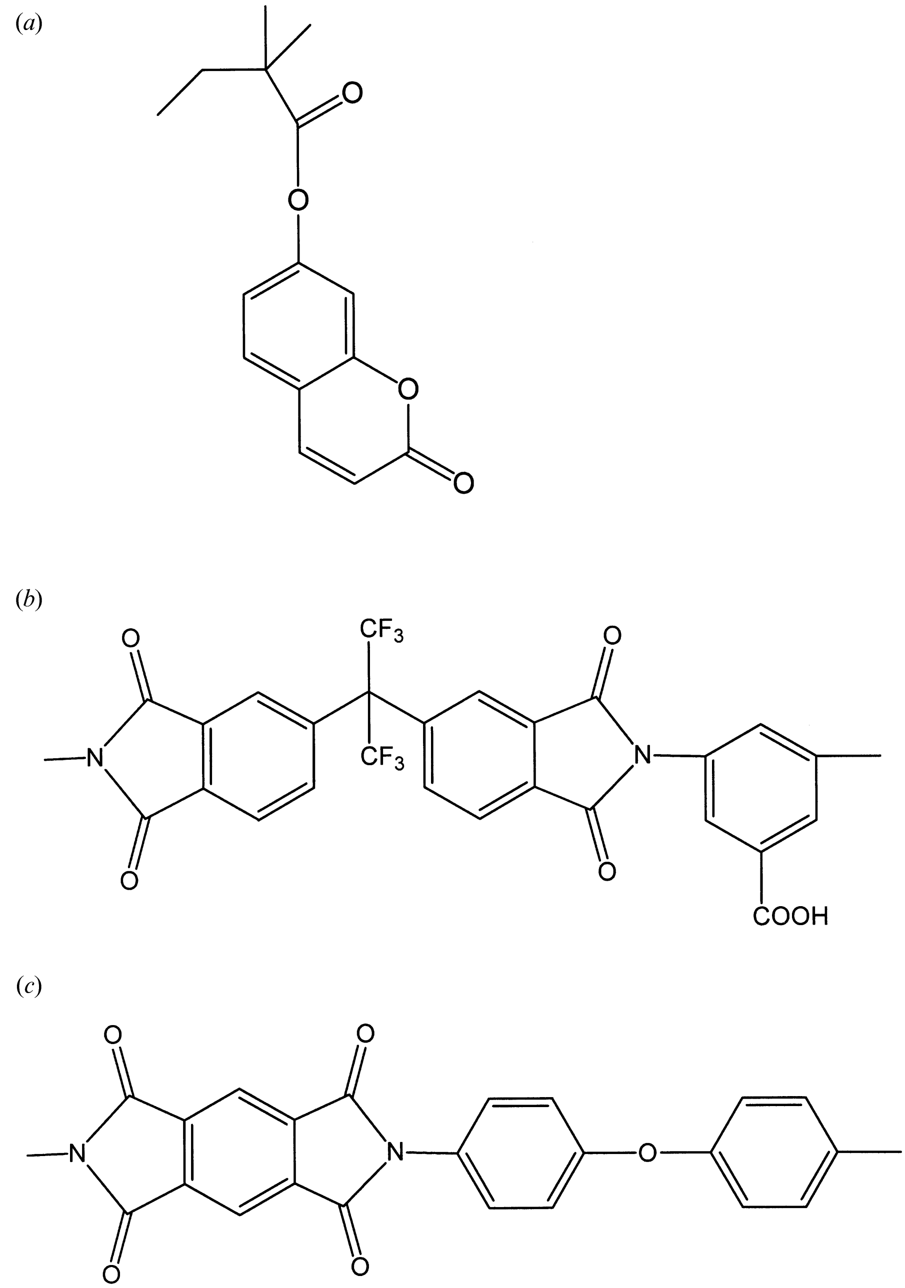

Figure 1. Chemical structures of the alignment materials (*a*) PMA-g-coumarin, (*b*) 6FDA-DBA, (*c*) PMDA-ODA.

a LC cell located between two crossed polarizers, the pretilt angles of nematic LC were determined.

3. Results and discussion

3.1. *Effect of polyimide on the LC orientation properties on blend alignment layers of PMA-g-coumarin and polyimide*

Figure 2 shows the polar plot of LC orientation on the alignment layers of PMA-*g*-coumarin as a function of thermal treatment temperature. The irradiation energy of the polarized UV was varied: 0.96 and 2.4 J cm^{-2}. When the LC cell was not thermally treated (65°C), the LC alignment was good and the direction of LC orientation was parallel to the polarization direction of the UV source [11]. However, in the case of thermal treatment at 150°C, the LC alignment was somewhat disordered while it was completely disrupted by thermal treatment at 200°C. The disorder of LC

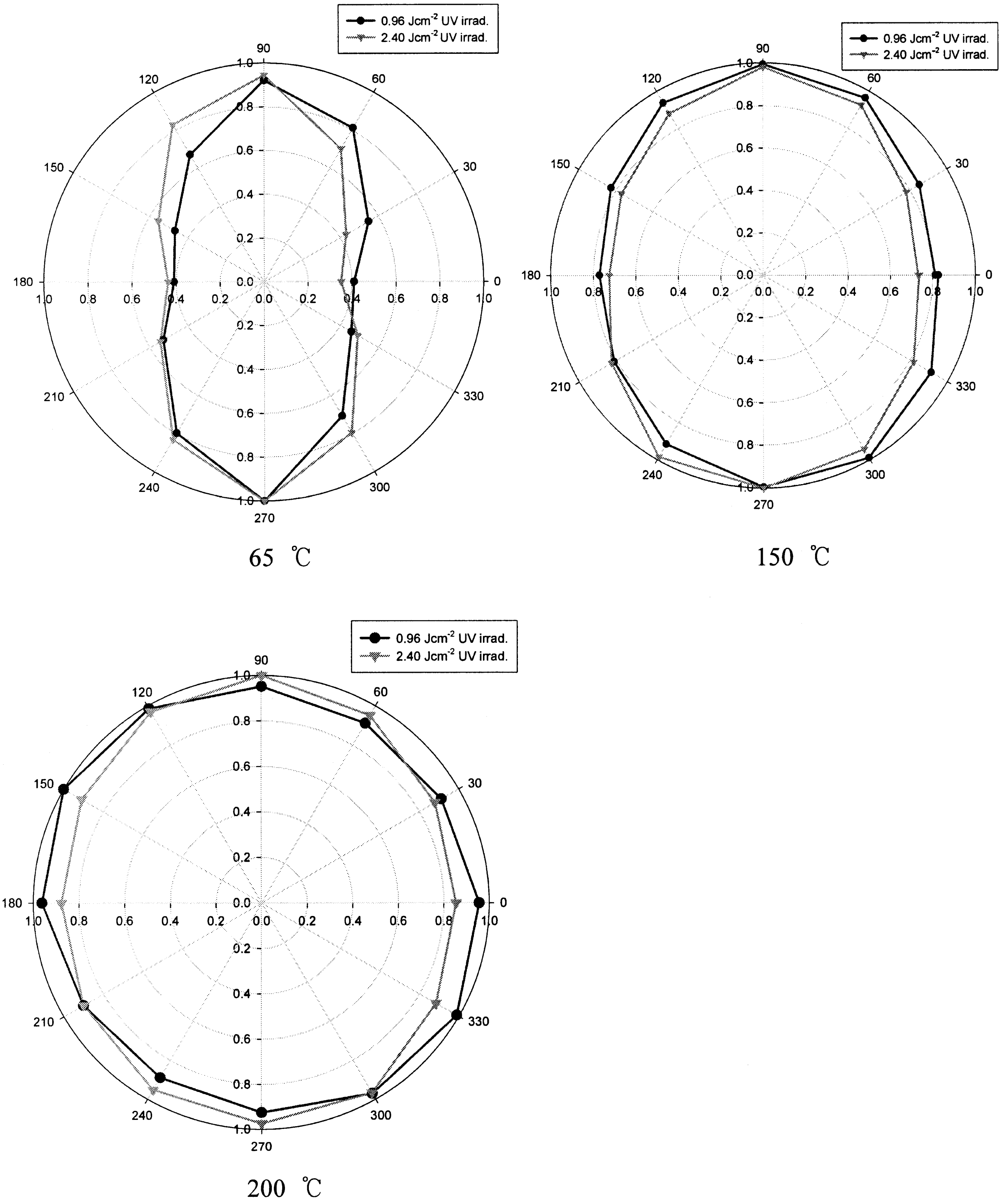

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Figure 2. Polar plot of LC orientation on the alignment layer of PMA-*g*-coumarin as a function of the thermal treatment temperature.

orientation induced by thermal treatment may be attributed to the low glass transition temperature, about 120°C, of PMA-*g*-coumarin.

In order to enhance the thermal stability of LC orientation on the PMA-*g*-coumarin alignment layer, we prepared the blend alignment layer contains PMA-*g*-coumarin and polyimides. We investigated the effect of the irradiation energy of the polarized UV, and of the thermal treatment, on the LC alignment properties of the blend alignment layer of PMA-*g*-coumarin and polyimides. Figure 3 shows the polar plot of LC orientation on the blend alignment layer of PMA-*g*-coumarin with (*a*) 6FDA-DBA, or (*b*) PMDA-ODA as a function of thermal treatment temperature.

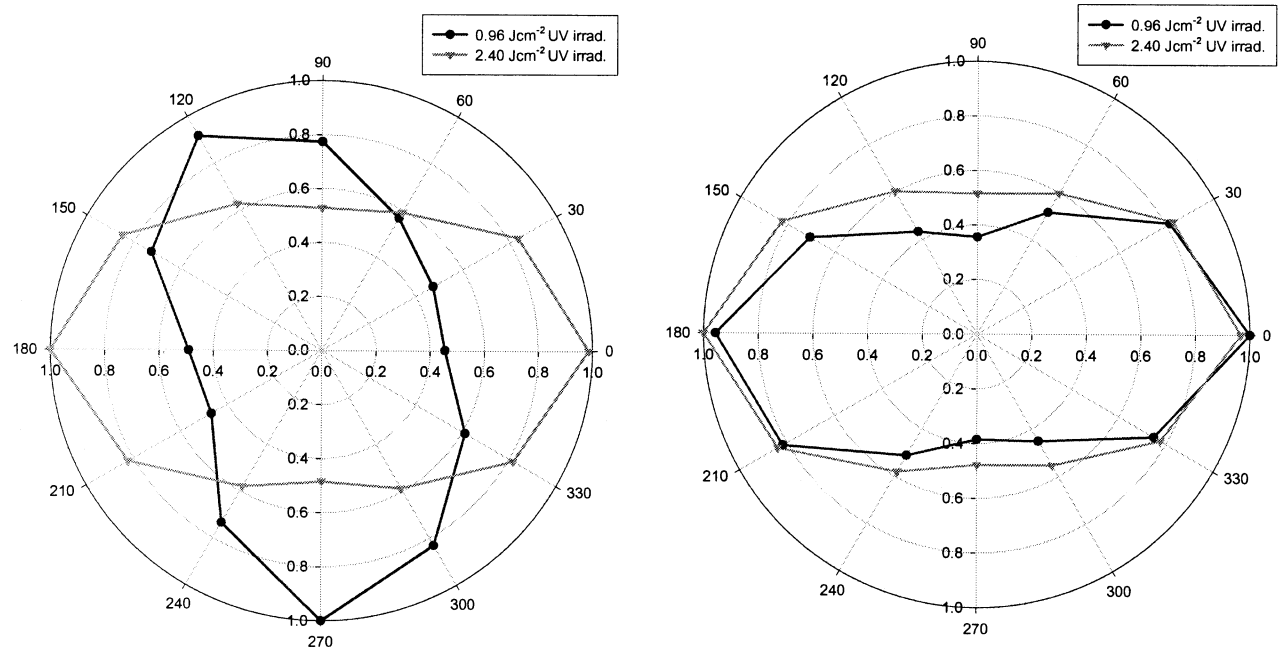
In the case of the blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA, the LC orientation was maintained after the thermal treatment at 200°C. However, the direction of LC orientation was different from that of PMA-*g*-coumarin. When the UV irradiation energy was $0.96\,\mathrm{J\,cm^{-2}}$, the direction of LC orientation was parallel to the polarization direction of the UV source. However, as the LC cell was thermally treated at 150°C and 200°C, the direction of LC orientation was changed from being parallel to perpendicular to the polarization direction of the UV source. Before thermal treatment of the LC cell, the anisotropic distribution of the photodimers of coumarin side chains determines the LC orientation due to the higher photoreactivity of coumarin side chains. However, thermal treatment of the LC cell randomizes the photodimers of the coumarin side chains due to the low thermal stability of PMA-*g*-coumarin. On the other hand, 6FDA-DBA polyimide is well known to be thermally stable above 200°C. Thus, the LC orientation was affected by the anisotropic distribution of the 6FDA-DBA chains. Generally, the LC alignment polyimide layer aligns the LC perpendicular to the polarization direction of the UV source. Therefore, the LC alignment direction on the blend alignment layer after thermal treatment was perpendicular to the polarization direction of the UV source. With a UV irradiation energy of $2.4\,\mathrm{J\,cm^{-2}}$, the direction of LC orientation was initially perpendicular to the polarization direction of the UV source and was not changed by thermal treatment. This result will be discussed in the next section.

In the case of the blend alignment layer of PMA-*g*-coumarin and PMDA-ODA, the LC orientation was stable after thermal treatment and the direction of LC orientation was not changed by the thermal treatment or UV irradiation. The direction of LC orientation is known to be an important factor for the generation of the pretilt angle [12]. Therefore, we checked the pretilt angle of the LC on the two blend alignment layers of PMA-*g*-coumarin and polyimide. The LC alignment layers which align the LC parallel to the polarization direction of the UV source are favourable for the generation of a pretilt angle. The pretilt angle of PMA-*g*-coumarin/PMDA-ODA was about 2.3° and almost 0° for PMA-*g*-coumarin/6FDA-DBA. The pretilt angle measurements supported the view that the low pretilt angle of PMA-*g*-coumarin/6FDA-DBA may be attributed to the perpendicular direction of LC orientation to the polarization direction of the UV source. The non-zero pretilt angle is required for the uniform display quality of an LCD and it is expected that PMDA-ODA is more suitable for the blend alignment layers of PMA-*g*-coumarin and polyimide.

3.2. *Relationship between photoreactivity of the polyimides and LC orientation on the blend alignment layers*

The direction of LC orientation on the blend alignment layers of PMA-*g*-coumarin and polyimide was affected by the type of polyimide in the blend alignment layers. The photoreactivity of alignment materials may influence the LC alignment properties. Therefore, we investigated the photoreactivity of PMA-*g*-coumarin, 6FDA-DBA, and PMDA-ODA by using UV spectrophotometry. Figure 4 shows the UV absorbance spectra of the polymer components of the blend alignment layers before UV irradiation and after 60 min UV irradiation. In the case of PMA-*g*-coumarin, the UV absorption spectrum showed absorption peaks in the range 250–350 nm, arising from the coumarin group. The reduction in the intensity of peaks after UV irradiation was remarkable, and implies the rapid disappearance of coumarin side chains by means of a higher photodimerization reaction. In the case of 6FDA-DBA, we observed that the absorption peaks in the range 200–300 nm and the intensity decrease of the absorption peaks caused by UV irradiation was smaller than that of PMA-*g*-coumarin. PMDA-ODA also shows absorption peaks in the range 200–300 nm, but the intensity decrease of the absorption peaks was less significant than that of PMA-*g*-coumarin or 6FDA-DBA. From these UV absorption spectra it is apparent that the photoreactivities of PMA-*g*-coumarin and 6FDA-DBA are higher than that of PMDA-ODA.

For the blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA, the photodimerization of coumarin and photodecomposition of the polyimide occur simultaneously and the LC alignment may be dominated by both of them (figure 5). PMA-*g*-coumarin showed higher photoreactivity than 6FDA-DBA. Thus, the LC alignment direction before thermal treatment is determined by the PMA-*g*-coumarin. After the thermal treatment, the LC orientation was dominated by the



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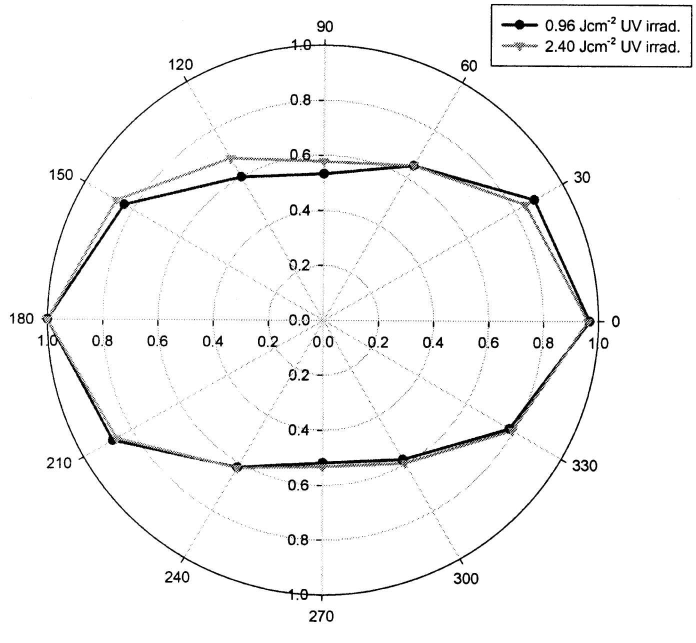

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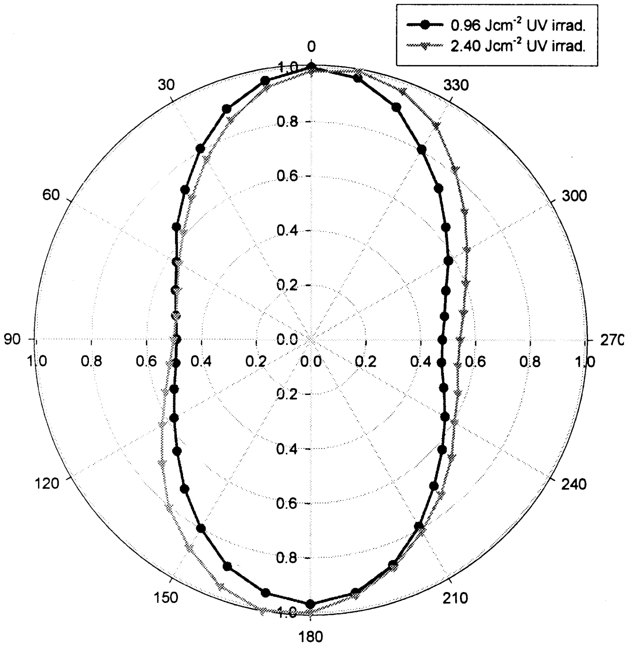
(*a*)

Figure 3. Polar plot of LC orientation on the blend alignment layer of PMA-*g*-coumarin and (*a*) 6FDA-DBA, (*b*) PMDA-ODA, as a function of thermal treatment temperature for 10 min.



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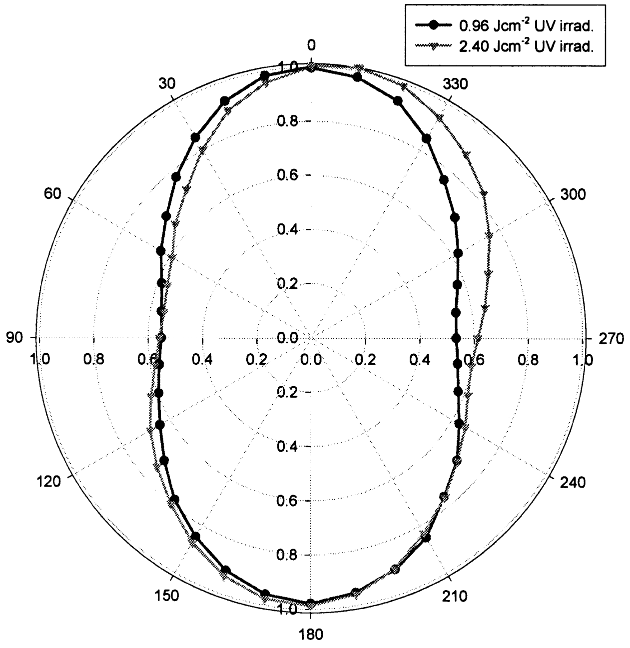

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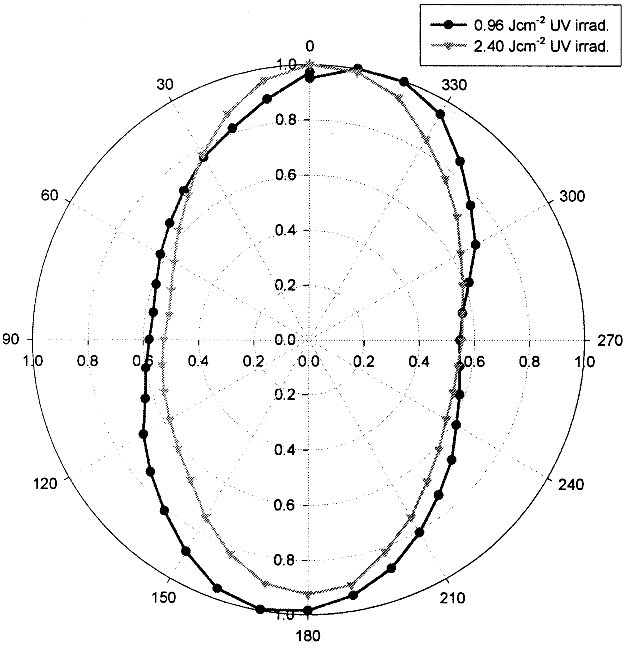

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(*b*)

Figure 3. (*Continued.*)

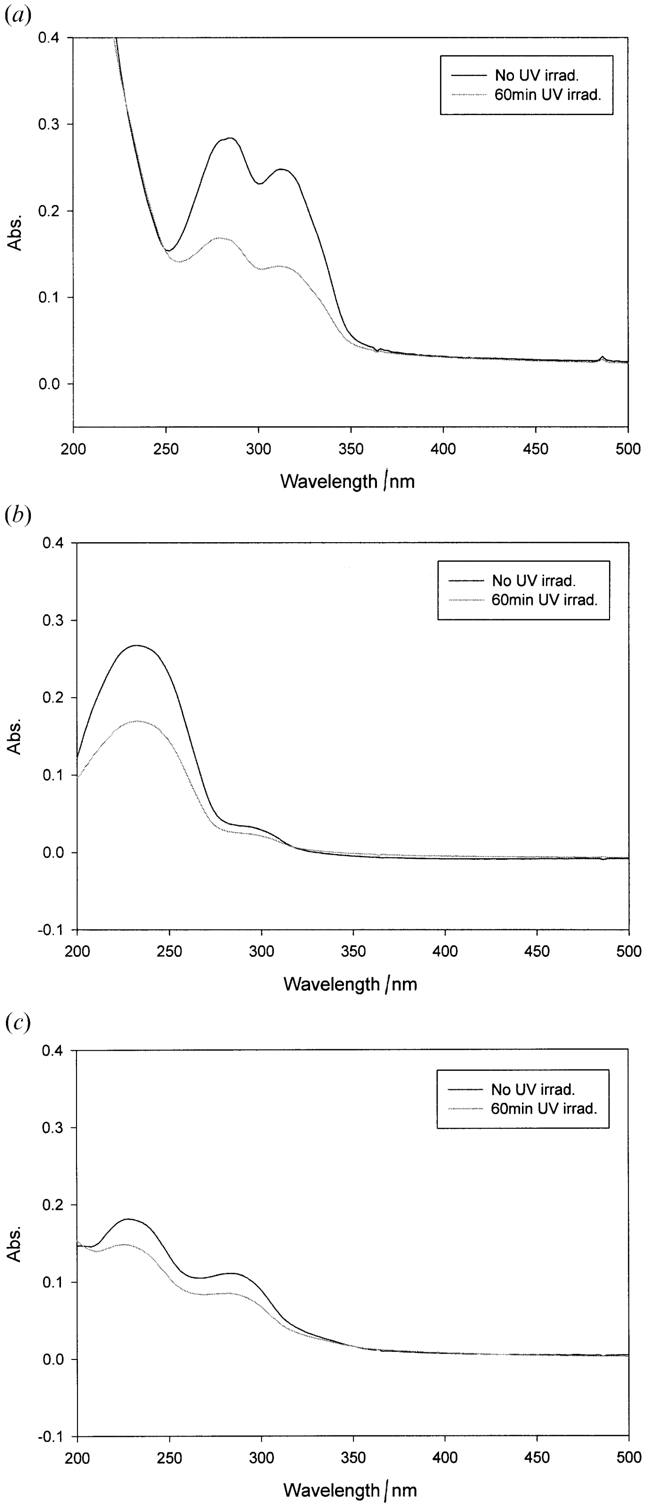

Figure 4. UV absorption spectra of (*a*) PMA-*g*-coumarin, (*b*) 6FDA-DBA and (*c*) PMDA-ODA before and after 60 min UV irradiation (UV filter 59800).

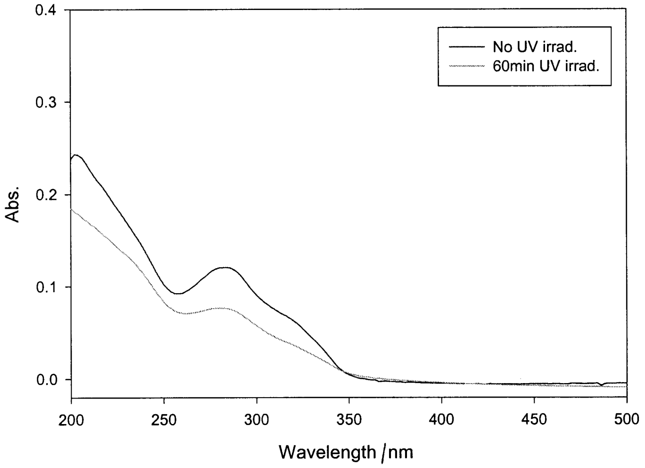

Figure 5. UV absorption spectra of the blend of PMA-*g*-coumarin and 6FDA-DBA before and after 60 min UV irradiation (UV filter 59800).

thermally stable 6FDA-DBA polyimide rather than by PMA-*g*-coumarin. The direction of LC orientation was changed to being perpendicular to the polarization direction of the UV source.

When the UV irradiation energy is increased to 2.4 J cm^{-2}, it was found that the direction of LC orientation on the blend alignment layer was perpendicular to the polarization direction of the UV source; this may be attributed to the difference in photoreactivity between PMA-*g*-coumarin and 6FDA-DBA. When the UV irradiation energy is reduced to 0.96 J cm^{-2}, the photodecomposition of 6FDA-DBA cannot be so significant and the LC orientation can be dominated by PMA-*g*-coumarin. However, when the UV irradiation energy is high, 2.4 J cm^{-2}, the photodecomposition of 6FDA-DBA becomes important and the LC orientation is determined by the 6FDA-DBA.

However, in the case of PMDA-ODA, the photodimerization reaction of coumarin side chains becomes dominant since PMDA-ODA is less photoreactive. Therefore, PMDA-ODA can maintain the LC alignment properties of PMA-*g*-coumarin after the process of thermal treatment, and this has little effect on the direction of LC orientation on the blend alignment layers. Because of the low photoreactivity of PMDA-ODA, the blend alignment layer of PMA-*g*-coumarin and PMDA-ODA could maintain the parallel LC orientation to the polarization direction to UV source despite the thermal treatment. In the blend alignment layer of PMA-*g*-coumarin and polyimide, the photoreactivity of polyimide is considered to be important in determining the direction of LC orientation after thermal treatment.

3.3. *Change of LC alignment properties by means of the wavelength of UV irradiation*

It was shown previously that the photoreactivity of the polyimide in the blend alignment layer exerted considerable influence on the LC orientation, including the thermal stability of LC orientation and its direction. In order to eliminate the effect of the polyimide on the LC orientation, the blend alignment layers were irradiated with polarized UV light of fixed wavelength that could only induce the photodimerization of coumarin side chains. From the UV absorption spectra of the alignment materials (figure 4), it was found that the wavelength band of main absorption peaks of PMA-*g*-coumarin and polyimides are different from each other. Thus, we used the UV filter 59610 that transmits only light in the range 295–305 nm instead of the UV filter 59800 transmitting in a wider rang 250–400 nm. Using this UV filter, only the photodimerization of coumarin side chains can occur and there would be no photodecomposition of the polyimides. Figure 6 shows the UV absorption spectra of 6FDA-DBA obtained by using UV filter 59610 as a function of irradiation time. In comparison with the UV absorption spectra obtained using UV filter 59800, there is no change in the absorption intensities even after 75 min UV irradiation, which means that UV irradiation in the range 295–305 nm does not trigger the photodecomposition of 6FDA-DBA.

We also prepared LC cells using a blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA irradiated by UV light filtered by UV filter 59610. Figure 7 shows the polar plot of the LC orientation on this blend alignment layer for different thermal treatment temperatures. The direction of LC orientation before thermal treatment was parallel to the polarization direction of the UV source, regardless of UV irradiation energy. After thermal treatment, the LC orientation was maintained and the direction of LC orientation was also maintained parallel to the polarization direction of the UV source. In this case, 6FDA-DBA shows no photodecomposition resulting from UV irradiation filtered by UV filter 59610. Therefore, there is no change of the direction of LC orientation on the blend alignment layers during thermal treatment. Pretilt angles can be generated because the direction of the LC orientation in coumarin is parallel to the polarization direction of the UV source [4]. The LC pretilt angle on the blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA using UV filter 59610 was 2.1° which is a much higher value than that of the blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA using UV filter 59800.

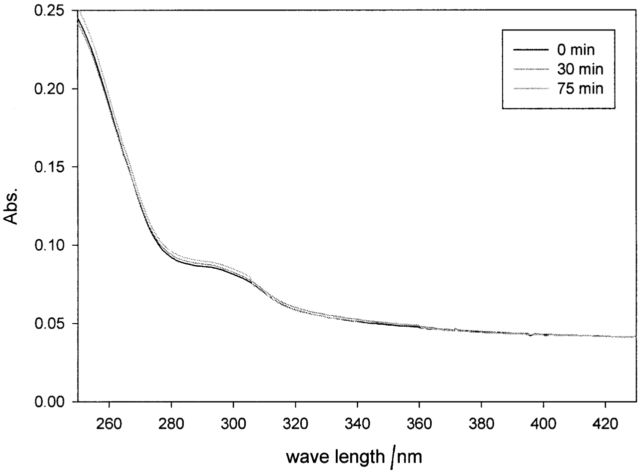

Figure 6. UV absorption spectra of 6FDA-DBA before and after 60 min UV irradiation (UV filter 59610).

From these results it is apparent that the degree of photoreaction of the polyimide in the blend alignment layer is a very important factor for LC orientation, and the direction of LC orientation can be controlled by adjusting the photoreaction of polyimide in the blend alignment layers. Polyimides can be used for the blend alignment layers to enhance thermal stability. However, polyimides with low photoreactivity are recommended for higher LC pretilt angle generation.

4. Conclusion

For the blend alignment layers of PMA-*g*-coumarin and polyimide, the thermal stability of LC orientation was enhanced by polyimide. However, the direction of LC orientation was affected by the photoreactivity of polyimides. In the case of the blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA, the direction of LC orientation was changed from parallel to perpendicular to the polarization direction of the UV source. The change of the direction of LC orientation may be attributed to the anisotropic decomposition of 6FDA-DBA due to the higher photoreactivity of 6FDA-DBA. However, the direction of LC orientation was not changed by thermal treatment and UV irradiation when PMDA-ODA of low photoreactivity was employed for the blend alignment layer. We could also control the photoreaction of 6FDA-DBA by changing the wavelength of transmitted UV light using appropriate UV filters. When the photoreaction of 6FDA-DBA was suppressed, the LC orientation of the blend of PMA-*g*-coumarin and 6FDA-DBA was similar to that of the blend of PMA-*g*-coumarin and PMDA-ODA. The pretilt angle of the LC cell was affected by the direction of LC orientation on blend alignment layers, and

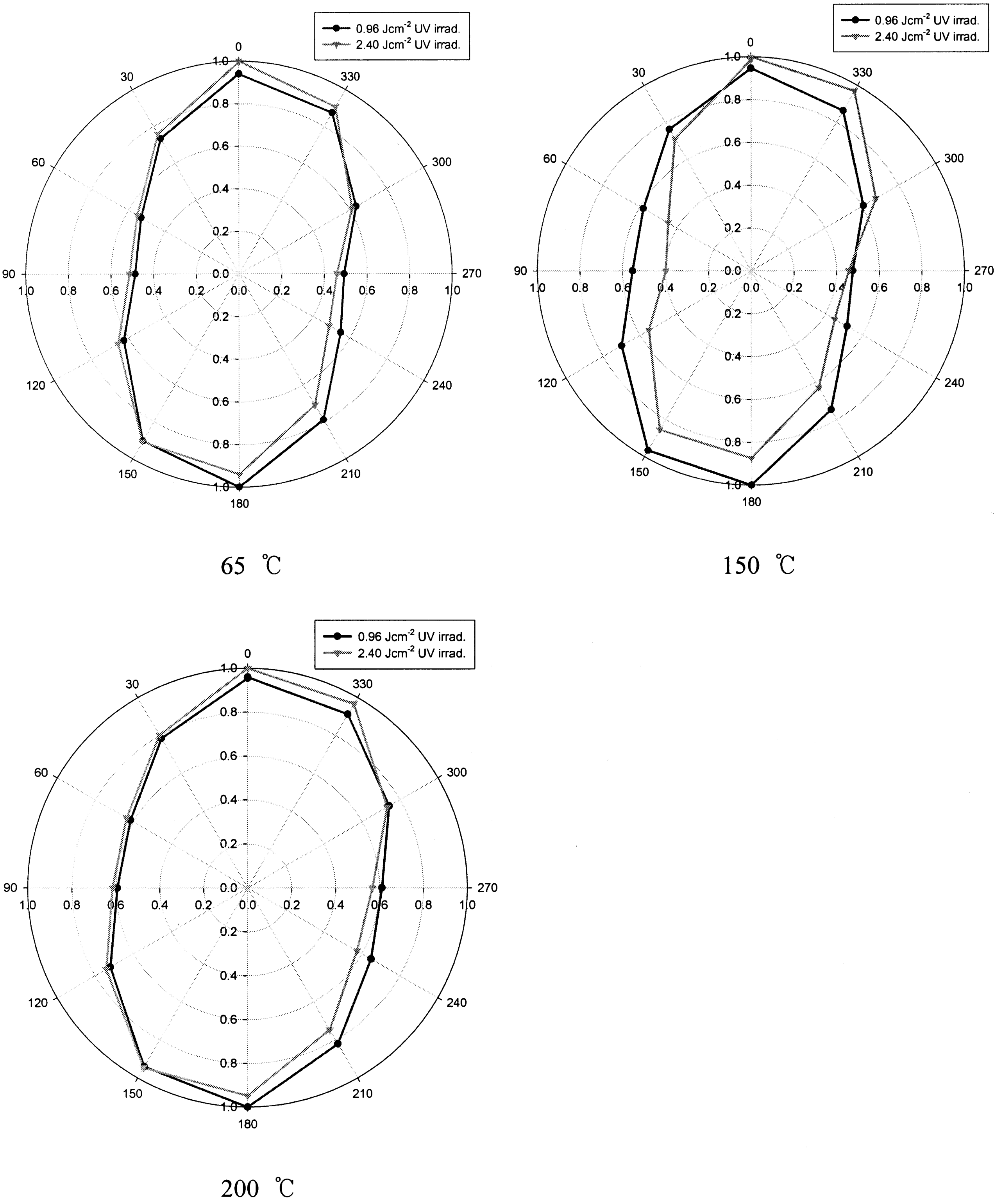

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Figure 7. Polar plot of LC orientation on the blend alignment layer of PMA-*g*-coumarin and 6FDA-DBA as a function of thermal treatment temperature (UV filter 59610).

polyimides with low photoreactivity are favourable for higher LC pretilt angle generation.

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